

Citric acid treatment of flax, cotton and blended nonwoven mats for copper ion absorption

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Abstract

The removal of metal ions from polluted water and wastewater with biodegradable, natural products is an area of current interest in the environmental arena. The objective of this study is to determine whether nonwoven mats made of biodegradable, natural fibers of flax and cotton can be used for remediation of a ubiquitous pollutant of water and wastewater, namely, copper ion. Nonwoven mats manufactured with flax or cotton fiber and flax/cotton fiber blends were treated with citric acid in order to enhance the amount of negative charge on the mats and improve their ability to sequester copper ion. The treated mats were monitored for changes in copper ion adsorption and fabric strength and compared to non-treated mats and process control mats. The results show that mats made from 100% flax and 75%/25% flax/cotton blends were similar to each other and significantly better at copper ion absorption than 100% cotton or 50%/50% flax/cotton blended nonwoven mats. Citric acid treatment, however, diminished mat strength compared to untreated mats for all samples; strength was similar for all treated nonwoven mats after correction for variable mat thickness. Treated flax fiber mats and flax/cotton fiber mats represent a potentially fast and convenient method for removal of metal ions from water and wastewater streams at an approximate cost of \$1.40/m² of mat.

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1. Introduction

Flax (*Linum usitatissimum* L.) is the source of high quality bast fibers from which linen fabric is produced. Linen is spun from long line flax, and production, cleaning, and processing are carried out under specific, time-consuming, and expensive methods. Shorter bast fibers produced either as tow (a by-product of long line flax production) or from the total plant, are blended

with cotton and other fibers for short staple spinning (McAlister et al., 2002; Sultana, 1992). Tow and total bast fibers are also considered for a variety of technical uses, such as paper/pulp, nonwoven mats, insulation and for reinforcement in composite materials (Van Dam et al., 1994).

Bast fibers comprise about 25% of the flax stem. Retting and processing to obtain flax fibers results in fibers with various characteristics. In addition to the long line fiber for linen, tow or total fiber can be shortened and refined, i.e., cottonized, for spinning in blends with cotton or other fibers on short staple systems. Tow, semi-cleaned, or cottonized flax fiber can also be manufactured into nonwoven mats either at 100% flax or in blends with

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other fibers, such as cotton (Annis et al., 2005). One use for a nonwoven, durable fabric in mat form could be as a filter for the entrapment of pollutants in water and wastewater. The non-treated mats could remove coarse particulates from a polluted source or they can be treated with a polycarboxylic acid, such as citric acid, to remove cationic pollutants, such as divalent metal ions, from solution.

Since flax fiber is lignocellulosic, the modification of the fiber with citric acid should result in improved divalent metal ion binding as has been shown for other lignocellulosic materials (Wing, 1996; Marshall et al., 1999; Wafwoyo et al., 1999; Vaughan et al., 2001). The potential advantage of a metal ion sequesterant in mat form from natural materials is that a nonwoven mat imposes rigidity on the material that would not be found in individual flax fibers in a column setting.

The objective of this study was to improve divalent metal ion binding of nonwoven mats composed of flax fiber or flax/cotton fibers by treatment with citric acid and compare both metal ion binding and fabric strength with mats not treated with citric acid.

2. Materials and methods

2.1. Materials

Flax was grown in the US in several regions for optimal fiber quality, dew-retted, baled, and stored. The bales were obtained from flax harvested over a period of several years and represented flax grown in initial commercial enterprises. Cultivars were not identified. The domestically grown and dew-retted flax was commercially processed through the Unified Line (Czech Flax Machinery, Merin, and Czech Republic), i.e., first-stage cleaning, and the fiber was subsequently cottonized, i.e., second-stage cleaning, all of which was carried out in Kingstree, SC. A second sample of flax fiber consisted of tow from a commercial source in Europe.

Cottonized flax fibers, which were from the stage two-cleaning at Kingstree, SC, and the imported tow were used for 100% flax mats. These two flax fiber types were also blended with two samples of domestically grown cotton fiber. One cotton sample was short-fiber waste gathered from vortex air jet spinning and had the following HVI properties: micronaire, 4.6; upper mean length, 2.25 mm; uniformity, 0.75%; strength, 30.1 g/tex; short fiber content, 14.1%; and elongation, 8.2%. The second cotton sample was from carded cotton sliver and had the following fiber properties: micronaire, 5.1; upper mean length, 2.56 mm; uniformity, 0.83%; strength, 28.0 g/tex; short fiber content, 9.7%; and elongation, 8.2%. The

fibers from sliver were fine and longer than the fibers discarded from air jet spinning.

Citric acid and other chemicals, which were reagent grade, were purchased from Fisher Chemical Co. (Pittsburgh, PA).

2.2. Methods

2.2.1. Mat production

Fibers were blended before carding and lapping prior to manufacture of nonwoven mats at Clemson University (Clemson, SC) as described (Annis et al., 2005). One hundred percent flax fiber mats using dew-retted flax processed commercially at Kingstree, SC, were prepared as single-layer, single-punched mats and as triple-layered, double-punched mats. In follow-up studies, two sets of nonwoven mats were made as described (Annis et al., 2005). In the first set, Unified Line-cleaned and cottonized flax and vortex spinning waste cotton fiber were used for four mats with the following initial blend levels: 100% flax, 75/25 flax/cotton, 50/50 flax/cotton, and 100% cotton. A second set of mats was manufactured from commercial flax tow from Europe and cotton sliver with the same fiber compositions as those for set one above. Mats of 10 cm × 10 cm were cut for treatment and analyses from the most uniform appearing sections of the mat. Mats had densities that varied from 0.040 g/cm² to 0.058 g/cm².

2.2.2. Citric acid treatment

The 10 cm × 10 cm mats were placed in shallow glass Petri dishes. Seven milliliters of 0.6 M citric acid (4.2 mmol citric acid) were added for each g of mat to give a w/v ratio of 1:7. For the water-treated mats, an amount of water corresponding to the amount of citric acid solution was added. All samples imbibed the added water or solution for one hr with little water or solution left in the dish. Both citric acid-treated and water-treated samples were dried at 60 °C overnight and then heated to 120 °C for 1.5 h. In order to remove non-reacted citric acid from the citric acid-treated mats, both citric acid-treated and water-treated samples were sealed in fiberglass screen pouches and washed with 3.0 L of water using an overhead stirrer for 1.5 h. The washed samples were dried at 60 °C overnight.

2.2.3. Strength and thickness tests

Tensile strength measurements were performed on the non-treated, water-treated and citric acid-treated mats using an Instron CRE tensile tester (Instron Corp., Norwood, MA) with pneumatic jaws, a gauge distance of 3–5 cm, a crosshead speed of 381 mm/min, and a 500 N

Table 1

Weight yield, copper ion adsorption and load at break for non-treated and treated flax fiber mats

Mat type ^a	Treatment	Weight ^b yield (%)	Copper ion ^c absorption (mmol/g)
Single-punched	Non-treated	NA ^d	0.10
	Water	89.4 ± 0.1	0.01
	Citric acid	121 ± 3	1.31 ± 0.14
Double-punched	Non-treated	NA ^d	0.00
	Water	90.5 ± 0.1	0.00
	Citric acid	111 ± 0	1.39 ± 0.10

^a Nonwoven mats made with dew-retted flax that was cleaned commercially through the Unified Line and then cottonized. Single-punched mats were 75% flax/25% cotton and one layer thick; double-punched mats were 100% flax and folded to form three layers.

^b Results represent the average of two replicates.

^c Results represent the average of two replicates for the citric acid-treated samples and one measurement for the water-treated and non-treated samples.

^d NA: not applicable.

load cell. Mats were cut into 2.5 cm × 10 cm ribbons and placed in the Instron. Tensile measurements were obtained using ASTM D 5035-03 (Standard Test Method for Breaking Force and Elongation of Textile Fabrics [Strip Method]) as described by Annis et al. (2005). Thickness of a test strip from each map was measured with a compressometer using ASTM D1777-02 (Standard Test Method for Thickness of Textile Materials). The strength at peak load and the strength of mats corrected for the variable thicknesses for the two flax/cotton fabrics were calculated for each set of mats, except that thicknesses were not measured for mats in Table 1. Values were compared within each group using a one-way analysis of variance, with least square differences (LSD) comparison.

2.2.4. Copper ion adsorption

Copper ion adsorption measurements were made on 0.25 g ribbons cut from the fiber mats. The 0.25 g ribbons were added to 25 mL of 20 mM copper chloride solution buffered at pH 4.8 with 0.02 M acetic acid and 0.03 M sodium acetate solution. The samples were stirred for 24 h at 300 rpm. The solutions were filtered through 0.45 µm filters and diluted in 4% Ultrex HNO₃. Copper ion in solution in both non-treated and treated samples was determined on the filtrates after suitable dilutions using a Leeman Labs Profile ICP-AES spectrometer (Leeman Labs, Hudson, NH) at 324 nm with an axial torch and dual view capabilities. All mats were dried to a moisture content of approximately 10% or less before ribbons were removed and adsorption analyses were conducted.

2.2.5. Scanning electron microscopy

Untreated and citric acid-treated nonwoven mats constructed with flax tow (Table 3) were evaluated for

structural changes after treatment with citric acid. A small fragment about 4 mm² was excised from one side of a swatch that had not been tested in the Instron to avoid any stresses imposed by the tensile testing equipment. This fragment was cut in half-longitudinally and the half-sections were mounted onto carbon stubs and sputter-coated with gold. The nonwoven samples were examined in a JEOL JSM 5800 Scanning Electron Microscope at 15 kV.

3. Results and discussion

3.1. Characteristics of flax fiber mats

Non-treated and water-treated, single-punched and double-punched (100% flax) mats adsorbed very little copper ion (Table 1). The single-punched mat made from 75% flax/25% cotton was used for tests, since 100% flax did not produce a uniform mat at this weight. The double-punched mat was made with 100% flax. Treatment of both types of mats with citric acid produced a large increase in metal ion adsorption and in product or weight yield (Table 1). There appeared to be only a slight and statistically insignificant difference between single-punched and double-punched mats in copper ion uptake, but product or weight yield was slightly higher for the single-punched mats. Product yields over 100% are due to the additional weight of reacted citric acid in the fiber. Product yields for the water-treated samples estimate the amount of fiber weight lost during fiber washing. Apparently mat weight played little if any role in the citric acid treatment process since single-punched, nonwoven mats were estimated to have an average density about 300 g/m², and the double-punched mats an average density of about 863 g/m² (unpublished data).

The effect of the citric acid treatment on flax fiber was considered to likely affect strength. In this preliminary test, tests for the load at break of the lighter, single punched mats, however, was extremely low and not different, giving some concern of the ability of the instrument to accurately detect any differences in strength for this fabric. The denser, double punched mats, which were stronger than the single-punched mats, showed a 52% reduction in strength for the citric acid-treated mats compared to the non-treated mats (data not included).

3.2. Characteristics of flax/cotton blend mats

Based on the preliminary strength results presented above, denser single-punched fiber mats made from 100% flax or cotton fibers and from fiber blends, of 5–6 mm thickness, were tested. Nonwoven mats using cotton fibers from vortex spinning wastes were used to determine the influence of non-scoured cotton alone and in blends with dew-retted flax processed through the Unified Line and cottonized. Flax, cotton, and flax/cotton-blended mats were subjected to similar treatments. Weight yields for the water-treated mats showed less than 10% loss of fiber due to the water wash (Table 2). Weight yields for the citric acid-treated mats were significantly higher when flax was present, especially 100% flax, compared to an all cotton mat. This may be a consequence of more citric acid reacting with the flax fiber than with the cotton fiber.

Copper absorption essentially occurred only with citric acid treatment (Table 2). With citric acid treatment, copper absorption was highest using nonwoven mats composed predominantly of 100% and 75% flax. Copper absorption using the 50% and 100% cotton mats was significantly ($p \leq 0.05$) reduced (Table 2) compared to the mats with higher flax content. The presence of significant amounts of cotton fiber in the mats diminished copper adsorption because the citric acid appears not to react effectively with the cotton. Since the cotton used is non-scoured, waxes surrounding the cotton fibers may impede the penetration of citric acid into the fiber and consequently reduce the reaction between citric acid and the cellulose component of the fiber. Flax, which is dew-retted and involves a partial degradation by aerobic fungi, may have its cellulose component more available to the acid for reaction than cotton. Further, the surface of cotton fiber appears to have more (or a different type) of wax from flax fibers (Akin et al., 2004; Himmelsbach et al., 2003), and this factor could influence citric acid uptake.

Citric acid significantly weakened flax-containing mats compared to non-treated mats as determined by tensile strength measurements (Table 2). The tensile strength of 100% cotton mats appeared unaffected by citric acid treatment compared to the non-treated and water-treated controls. A reduction in flax content of the mats significantly diminished the strength of the non-citric acid-treated mats (Table 2). However, there was no significant difference in fabric strength among the cit-

Table 2
Weight yield, copper ion adsorption and strength of mats from non-treated and treated flax, cotton and flax/cotton blends^a

Mat type	Treatment	Weight yield ^b (%)	Copper ion absorption ^c (mmol/g)	Strength at peak load ^d (N)	Thickness ^e (mm)	Strength corrected for fabric thickness (N/mm)
Flax: 100%	Non-treated	NA	0.10	36.9 ± 2.2 b	4.1 ± 0.2 a	9.0 ± 0.9 b
	Water	91	0.05	47.6 ± 12.2 a	3.5 ± 0.5 c	13.5 ± 2.3 a
	Citric acid	119 ± 3 a	1.06 ± 0.18 a	15.8 ± 3.7 d	4.1 ± 0.4 a	3.8 ± 0.8 e
Flax/cotton: 75/25	Non-treated	NA	0.13	30.3 ± 8.8 c	3.9 ± 0.2 ab	7.6 ± 1.9 cd
	Water	91	0.15	32.8 ± 4.4 c	3.9 ± 0.1 abc	8.4 ± 1.2 c
	Citric acid	111 ± 1 b	1.16 ± 0.06 a	16.1 ± 1.9 d	4.0 ± 0.2 ab	4.0 ± 0.5 e
Flax/cotton: 50/50	Non-treated	NA	0.11	28.9 ± 2.4 c	3.9 ± 0.1 ab	7.3 ± 0.5 d
	Water	91	0.16	30.5 ± 7.3 c	3.7 ± 0.2 bc	8.2 ± 1.7 cd
	Citric acid	110 ± 3 b	0.83 ± 0.15 b	16.3 ± 1.6 d	4.1 ± 0.3 a	4.0 ± 0.4 e
Cotton: 100%	Non-treated	NA	0.01	12.9 ± 2.5 d	3.8 ± 0.1 abc	3.4 ± 0.6 e
	Water	95	0.04	12.3 ± 5.6 d	3.7 ± 0.3 bc	3.2 ± 1.3 e
	Citric acid	103 ± 3 c	0.54 ± 0.22 c	13.9 ± 2.8 d	4.1 ± 0.3 a	3.4 ± 0.6 e

Values within columns with different letters differ at $p \leq 0.05$ using one-way analysis of variance.

^a Mats constructed with total fiber from dew-retted flax processed through the Unified Line and cottonized and vortex cotton spinning wastes.

^b Average of two replicates for the citric acid-treated samples and one measurement for the water-treated and non-treated samples.

^c Average of two replicates for the citric acid-treated samples and one measurement for the water-treated and non-treated samples.

^d Average of 10 replicates.

^e Average of 10 replicates.

ric acid-treated mats at any flax or cotton content. Since citric acid treatment of flax or cotton fiber imparts a negative charge on the fiber due to the carboxylic groups from citric acid, a specific amount of negative charge may cause adjacent fibers in the mats to repel one another and subsequently reduce strength to a minimum.

In order to determine whether the results and trends associated with blended fiber mats in Table 2 were applicable to blended fiber mats made with different types of flax and cotton fiber, another series of flax, cotton and flax/cotton mats were produced. Instead of using dew-retted flax processed through the Unified Line and cottonized, mats were made from commercial flax tow. The type of cotton was also changed from vortex-spun cotton waste to carded cotton sliver. In both cases the type of fiber used was changed to reflect the use of readily available commercial material (Table 3).

Weight loss from water washing the mats was under 10% as observed previously for fabrics in Table 2. Percent weight yields for citric acid-treated mats decreased with an increase of cotton content, and this result was associated with a decrease in copper adsorption as seen with the mats in Table 2. The mats made with commercial flax tow removed more copper from solution than any other mat examined, and in general mats made with flax tow and/or cotton sliver (Table 3) had higher copper adsorption than mats made with cottonized flax and vortex spun cotton (Table 2).

Mat strength was again lower in mats treated with citric acid compared to non-treated or water-treated samples (Table 3). These reduced values were comparable to the values determined in Table 2, especially when mat strength was corrected for variable fabric thickness. Scanning electron microscopy (Fig. 1) showed intact flax fibers within the nonwoven mat after citric acid treatment, indicating that substantial visible fiber destruction had not occurred although fiber strength reduction was relatively high. These results lend support to the contention that under specific conditions of citric acid treatment, mat strength may reach a minimum value of about 3.5–4.0 N/mm.

3.3. Product cost

An estimate of product (mat) cost is based on additive costs for fiber material, mat manufacturing and citric acid treatment. Product cost would vary based on mat thickness, since more fiber would be required for a thicker mat. In the example used, a 5 mm thick mat is assumed with an approximate density of 0.58 kg/m². The cost of commercial flax or cotton used in this study is estimated at \$0.66 kg⁻¹. To manufacture 1.0 kg of fiber into mats would cost approximately \$0.88 (Kyle Gipson, personal communication). Finally, the cost to treat the mats with citric acid is estimated to be \$0.88 kg⁻¹ based on the treatment process and cost given by Marshall et al. (2001)

Table 3

Weight yield, copper ion adsorption and strength measurements of mats from non-treated and treated flax, cotton and flax/cotton blends^a

Mat type	Treatment	Weight yield ^b (%)	Copper ion absorption ^c (mmol/g)	Strength at peak load ^d (N)	Thickness ^e (mm)	Strength corrected for fabric thickness (N/mm)
Flax: 100%	Non-treated	NA ^f	0.03	26.1 ± 6.8 ef	5.4 ± 0.1 b	4.9 ± 1.2 cde
	Water	94	ND ^g	52.4 ± 12.2 a	5.2 ± 0.2 bc	10.0 ± 2.2 a
	Citric acid	115 ± 2 a	1.30 ± 0.01 a	19.2 ± 3.4 gh	4.7 ± 0.4 cd	4.1 ± 0.7 de
Flax/cotton: 75/25	Non-treated	NA	0.03	22.2 ± 2.4 fg	4.0 ± 0.1 e	5.5 ± 0.7 c
	Water	91	0.03	32.6 ± 1.7 c	4.1 ± 0.1 de	7.9 ± 0.5 b
	Citric acid	113 ± 3 ab	1.18 ± 0.07 a	14.8 ± 1.3 h	4.1 ± 0.5 e	3.7 ± 0.6 e
Flax/cotton: 50/50	Non-treated	NA	ND	17.5 ± 3.7 gh	3.4 ± 0.1 f	5.2 ± 1.3 cd
	Water	91	ND	32.1 ± 1.0 cd	3.9 ± 0.3 ef	8.3 ± 0.8 b
	Citric acid	109 ± 5 bc	0.68 ± 0.17 b	13.7 ± 2.1 h	3.9 ± 0.3 ef	3.5 ± 0.5 e
Cotton: 100%	Non-treated	NA	0.01	42.1 ± 3.3 b	5.5 ± 0.1 b	7.7 ± 0.7 b
	Water	94	0.04	40.9 ± 5.6 b	5.4 ± 0.1 b	7.6 ± 0.9 b
	Citric acid	105 ± 2 c	0.80 ± 0.15 b	25.8 ± 1.5 ef	6.0 ± 0.4 a	4.3 ± 0.3 cde

Values within columns with different letters differ at $p \leq 0.05$ using one-way analysis of variance.

^a Mats constructed with commercial flax tow from dew-retted flax and with cotton sliver.

^b Average of two replicates for the citric acid-treated samples and one measurement for the water-treated and non-treated samples.

^c Average of two replicates for the citric acid-treated samples and one measurement for the water-treated and non-treated samples.

^d Average of 10 replicates.

^e Average of 10 replicates.

^f NA: not applicable.

^g ND: copper absorption not detectable at a concentration <0.01 mmol/g.

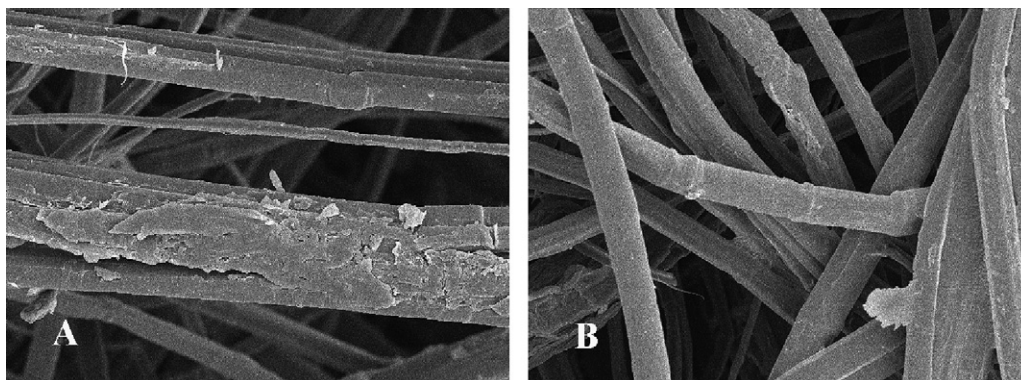


Fig. 1. Scanning electron micrographs of 100% flax nonwoven mats, 500 \times . (A) Untreated mat and (B) citric acid-treated. Fibers appear intact after citric acid treatment, indicating no substantial visual destruction of fiber structure.

with changes made in the process to accommodate fiber mats rather than soybean hulls. Additive cost for the finished product would be about \$2.42 kg⁻¹. However, the density of the mat in question is 0.58 kg/m², so 1.0 m² would cost \$1.40 for treated mat.

4. Conclusions

Treatment with citric acid resulted in a significant improvement in copper ion absorption for flax and/or cotton fiber nonwoven mats where the flax and cotton were obtained from diverse sources. Flax fiber mats containing 100% flax and 75%/25% flax/cotton blends were significantly better in copper ion absorption than 100% cotton or 50%/50% flax/cotton blends. Significant strength loss occurred in the citric acid-treated mats, except with the 100% cotton mats where no loss was observed when correction was made for variable mat thickness. This strength loss could not be explained by morphological examination of the fibers using scanning electron microscopy.

Citric acid treated flax mats or mats with a predominant flax content appear to be very effective at copper ion adsorption and could be used in locations where use of column filters for metals removal would be difficult, such as in storm water filtration. However, the diminution in fabric strength after treatment would have to be reconciled in field evaluations of the mats.

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References

- Akin, D.E., Rigsby, L.L., Morrison III, W.H., 2004. Oil Red as a histochemical stain for natural fibers and plant cuticle. *Ind. Crops Prod.* 19, 119–124.
- Annis, P.A., Brewer, M.S., Akin, D.E., Dodd, R.B., Foulk, J.A., Vaughn, E.A., Knopp, J.A., 2005. Cotton-flax blended nonwoven fabrics with value added properties for industrial markets. In: *Proceedings of the 2005 Beltwide Cotton Conferences*, New Orleans, LA, pp. 2780–2786.
- Himmelsbach, D.S., Akin, D.E., Kim, J., Hardin, I.R., 2003. Chemical structural investigation of the cotton fiber base and associated seed coat: Fourier-transform infrared mapping and histochemistry. *Textile Res. J.* 73, 281–288.
- Marshall, W.E., Wartelle, L.H., Boler, D.E., Johns, M.M., Toles, C.A., 1999. Enhanced metal adsorption by soybean hulls modified with citric acid. *Bioresour. Technol.* 69, 263–268.
- Marshall, W.E., Chatters, A.Z., Wartelle, L.H., McAloon, A., 2001. Optimization and estimated production cost of a citric acid-modified soybean hull ion exchanger. *Ind. Crops Prod.* 14, 191–199.
- McAlister III, D.D., Foulk, J.A., Akin, D.E., Annis, P.A., 2002. Cotton fibers: properties and interaction with flax fibers in blends. In: *Proceedings of the 26th International Cotton Conference* Bremen, Faserinstitut Bremen, Germany, pp. 207–211.
- Sultana, C., Scutching of retted-flax straw, 1992. In: Sharma, H.S.S., Van Sumere, C.F. (Eds.), *The Biology and Processing Of Flax*. M Publications, Belfast, Northern Ireland, pp. 261–274.
- Van Dam, J.E.G., van Vilsteren, G.E.T., Zomers, F.H.A., Shannon, W.B., Hamilton, I.T., 1994. *Industrial Fibre Crops: Increased Application of Domestically Produced Plant Fibres in Textiles, Pulp and Paper Production, and Composite Materials*. ATO-DLO, Wageningen, The Netherlands.
- Vaughan, T., Seo, C.W., Marshall, W.E., 2001. Removal of selected metal ions from aqueous solution using modified corn cobs. *Biore-sour. Technol.* 78, 133–139.
- Wafwoyo, W., Seo, C.W., Marshall, W.E., 1999. Utilization of peanut shells as adsorbents for selected metals. *J. Chem. Technol. Biotechnol.* 74, 1117–1121.
- Wing, R.E., 1996. Corn fiber citrate: preparation and ion exchange properties. *Ind. Crops Prod.* 5, 301–305.